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THE NATURE OF THE INTERFACES EXISTING IN THE PORES OF SILICA GEL

AND

THE RETENTION OF BROMINE BY SILICA GELS.

DISSERTATION

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DOCTOR OF PHILOSOPHY

BY

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THE NATURE OF THE INTERFACIAL FILMS IN THE PORES OF SILICA GEL AND THE RETENTION OF BROMINE BY SILICA GELS.

The following investigation was undertaken for the purpose of more definitely establishing the mechanism of the adsorption and retention of gases and liquids by silicic acid gels.

It has been well established by Zsigmondy and his coworkers(1) that the hydrate theory of silica gel is no longer tenable. In the absence of air he was able to measure the adsorption of alcohol and benzol. He obtained curves very similar to van Bemmelen's curves for water. It does not seem possible that the gel structure should form even a loose combination with such a material as benzol. It was further shown that the dry gel only took up the various liquids in proportion to the existing free spaces. Zsigmondy's work thus leaves little basis for the theory of chemical union between the gel and the liquids taken up.

It became necessary on the basis of this work to show rather definitely the actual structure of the gel. Bütschli(2) concluded from his microscopic studies of silica gel that the pores of the gel were of microscopic dimensions. From ultra microscopic studies Zsigmondy and Bachmann(3) were able to disprove this view. The heterogeneity, which Bütschli mistook for gel pores, were shown to be numerous small bubbles. The optical homogeneity of the dry gel and the action toward colloidal solutions show definitely that the dimensions of the gel pores lie well below the limit of microscopic visibility.

The extreme fineness of the gel pores led Zeigmondy and his co-workers to employ the considerations of capillary theory to the phenomena in question. The theory advanced on the basis of capillary structure explains in a satisfactory way the properties of the gel.

The extreme state of subdivision gives the gel a large inner surface and it is probable that the first gases or vapors taken up by the gel are adsorbed on this surface. In addition from the well known considerations of capillary phenomena it is possible to explain the filling of the gel pores. On the basis of capillary theory the equilibrium vapor pressure in the fine pores over the condensed phase would be less than the ordinary vapor pressure above the same condensed material. Thus the pores would be filling under a reduced pressure until equilibrium between the vapor phase within and without the pores is established.

Anderson(4) was able to quantitatively prove these theories, measuring the amounts of water, alcohol and benzol taken up under various pressures. He calculated the values for the radius of the pores at the 0 point of the Van Bemmelen curve and they showed very good agreement for the three liquids. He found the average diameter to be not far from 5$\mu\mu$. This agrees very well with the ultra microscopic properties and with the behavior of the gel toward colloidal silver.

Patrick(5) investigated the properties of the gel further using the gases SO_2 and NH_3 at various temperatures. Above the boiling point of these materials the capillary theories were not applicable because other factors interferred. Up to the point at which condensation in the gel might occur the formulae based on the

capillary theory were applicable.

The foregoing investigations have shown that silica gel is a very porous material and that the capillaries were of the order of 5×10^{-7} cm. in diameter. On the basis of capillary theory the results of the above investigations indicate very strongly that the surface of the condensed phase is concave toward the vapor phase. This means that the condensed phase wets the walls of the capillaries. If this be so then it should be possible to show a decreased solubility for materials in the gel just as Hulett was able to show a decided increase in solubility of $BaSO_4$ when the radius of the convex surface became small enough.

Accordingly a very good sample of the silica gel with a water content of about eight per cent was completely filled with bromine by allowing it to come in contact with saturated bromine vapors. The gel became a dark garnet red during the exposure. If this bromine could be retained by the gel when in contact with water, then according to the theory bromine should be less soluble from the gel than it is when free liquid bromine is in contact with water. To prove this fact the gel saturated with bromine was covered with water. Instead of dissolving slowly as was expected the bromine came out of the gel almost instantly and collected in small drops throughout the gel mass. The process was accompanied by considerable evolution of heat and the gel became perfectly colorless once more showing that the bromine had been completely displaced by the water.

This phenomena can of course be accounted for on the basis of surface tension, the surface tension between the water-gel interface being greater than that between the bromine-gel interface. The greater surface tension of the water-gel interface would cause the water to creep into the pores between the surface of the gel and the bromine, finally forcing the bromine out of the pores. The energy changes of surface may account for the heat effects.

The same experiments were repeated with iodine. It was thought that the iodine being a solid would not be displaced by the water but such was not the case. The iodine was forced out of the gel and formed well defined crystals on the walls of the containing vessel. This would seem to indicate that the surface tension between the solid interface iodine-gel, was less than that between the interface water-gel. This fact will bear further investigation.

As a result of these experiments it was deemed wise to measure the adsorption of bromine by the silica gel and obtain if possible some insight into the mechanism of the adsorption and retention of the bromine by the gel. Furthermore, a study of the solubility of water from the gel in some such liquid as ether would clear up in all probability the questions of surface tension and the wetting of the surface of the pores.

A study was then made of the adsorption of bromine by silica gels of varying water content at 40°C, 25°C and 10°C.

METHOD OF EXPERIMENTATION.

The Silica Gel:

The silica gel used in this investigation came from a large sample which was made on a semi-commercial scale. It was prepared in the usual way by running equal amounts of tenth normal sodium silicate into tenth normal hydrochloric acid and allowing the gel to set. The wet gel was then dialized until the effluent water gave no chloride test. It was then dried and broken up to about 12-20 mesh material. This gel before further treatment contained about six per cent water by weight and was a light creamy white in color. The gel at this point has considerable impurities present in the form of organic matter. This is removed by filling the pores of the gel with oxides of nitrogen obtained by boiling concentrated nitric acid. The gel is dialized once more to remove electrolytes and dried.

At this point the gel is dried at a temperature of about 110° Centigrade for several hours. This produces a gel with a water content of about sixteen per cent. In order to produce a good quality of clear white gels with less water than sixteen per cent it is necessary to dry the gel at a higher temperature in a stream of dry air. A good vacuum with higher temperatures produces a good quality of gel but experience has shown that the air dried gels are slightly better. Temperatures

above 500°Centigrade are necessary to produce gels with a water content below four to five per cent. As will be shown later, gels with a water content less than four or five percent do not take up gases and vapors as well as those with four per cent or more water.

The water content of the gel was determined by finely grinding the gel in a mortar. Then a sample of this powdered gel was heated in a platinum crucible to constant weight. The loss in weight of the gel was taken as the loss of water.

THE DESCRIPTION OF THE APPARATUS USED.

The method employed in carrying out the measurements was a colorimetric method. Figure No.I gives a diagramatic sketch of the apparatus. Two tubes, A and B, were blown from the same sized glass tubing. Tube A was closed at both ends while tube B was left open at one end. Tube C was blown so that it fitted well into the inside of B with enough play so that tube C could be moved back and forth as a plunger in B without difficulty. Tube C was covered with paraffin and marked with a dividing engine. The tube was then etched with the zero reading at the hump. The arrangement was such that, with the closed end of tube C touching the closed end of tube B, the reading on tube C was zero. A small nipple of about 4 c.c. capacity was blown on the sides of tube B near the closed end of the tube. Directly opposite the nipple a ground glass stopper was constructed. This stopper allowed the introduction of liquid bromine into the nipple of tube B. A similar nipple and stopper were constructed near one end of tube A. This was used to introduce both bromine and silica gel into tube A.

Tubes A and B were carried parallel in a specially constructed air thermostat. Holes, the size of the tubes, were cut in both ends of the thermostat to allow the passage of light through the tubes to the colorimeter. The end of the

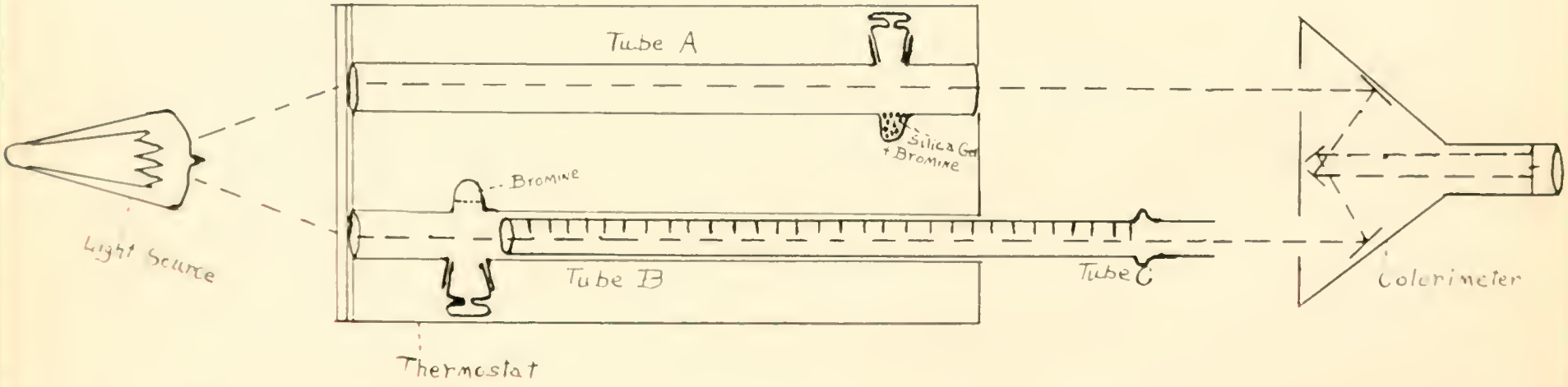


Diagram of Adsorption Apparatus

thermostat nearest the light source was covered with a piece of frosted glass and the light source was a frosted 150 watt nitrogen light.

The top of a Duboscq colorimeter, including the telescopic eyepiece and the mirror device which brings the two light beams onto the divided field, was removed from the base of the colorimeter and mounted on a standard parallel to the tubes A and B so that the light beams through A and B were caught and focused on the divided field.

The Method of Procedure:

The experimentation was carried out as follows: Liquid bromine was introduced into the nipple of tube B in sufficient quantity to constantly assure a saturated bromine vapor in B and the stopper inserted. Tube C was then pushed part way into tube B and both tubes placed in the thermostat. From 3 to 5 grams of silica gel were weighed into the nipple of tube A. A known weight of bromine was then added and the stopper inserted. The gel was shaken through the tube to insure rapid attainment of equilibrium and the tube was placed beside tube B in the thermostat. A fan of the blower type forced air from a coil in a water thermostat through the air thermostat and a constant temperature was soon reached.

Tube C was moved slowly back and forth in tube B until the two color fields in the colorimeter matched. The value read off on tube C gave the number of centimeters of saturated bromine vapor which correspond to the total length

of the tube of unsaturated vapor. The ratio of the two lengths gives the vapor pressure of the bromine over the silica gel.

The color could be matched within the length of a tenth of a centimeter in the movement of tube C. The color matching was always made with tube C coming from both sides to the point of equilibrium. The mean value taken was always the result of several color matchings.

After the color had been matched for the first bromine added to the gel, additional bromine was weighed into tube A from a weight burette. After equilibrium had been reached the color was again matched. This was repeated six or seven times until the vapor pressure of the bromine in tube A had nearly reached that of liquid bromine at that temperature. These values gave the necessary data for the calculation of results.

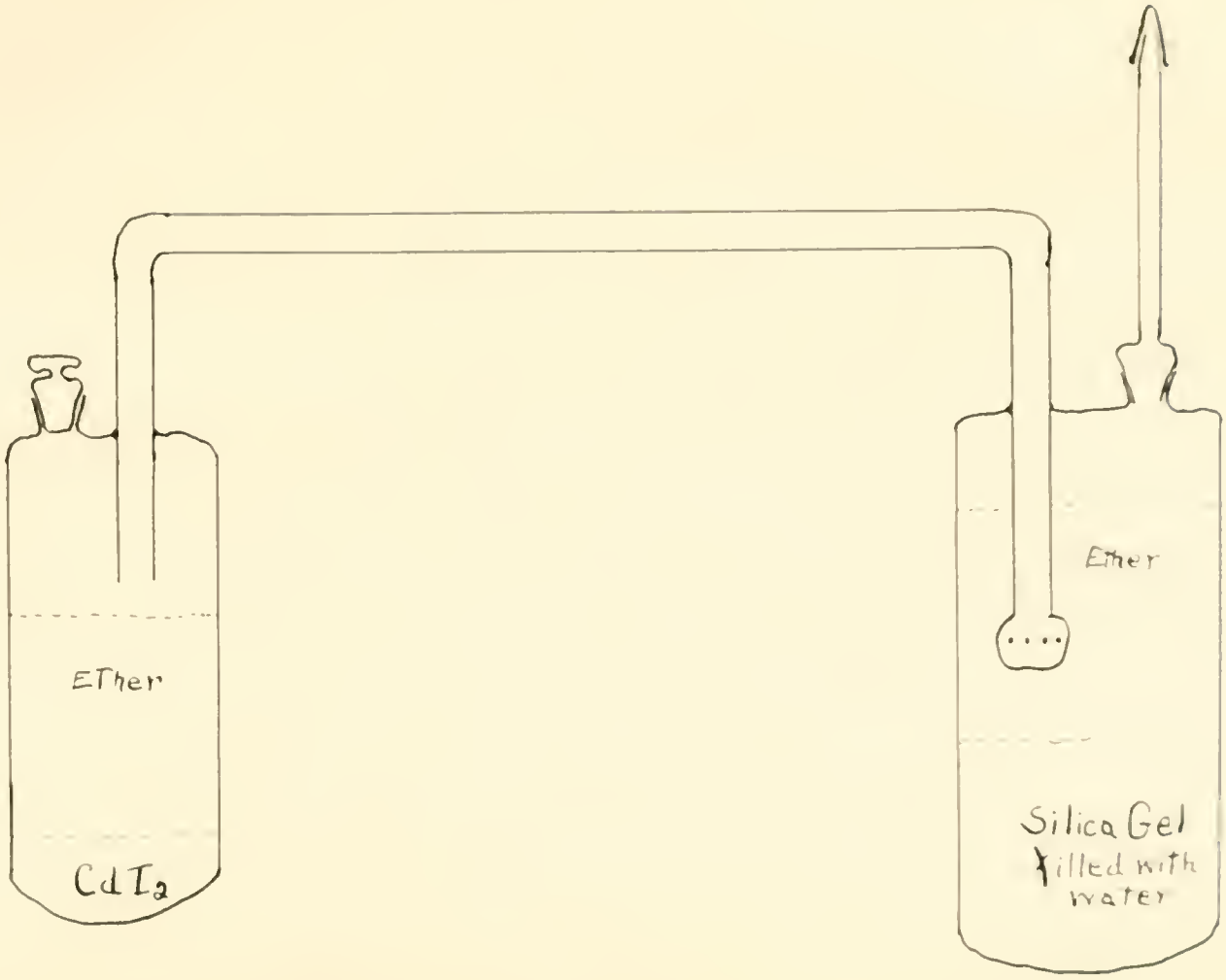
THE DETERMINATION OF THE SOLUBILITY OF WATER FROM SILICA GEL IN ETHER.

The Ether:

The ether was washed several times with calcium chloride solution and once with sodium nitrite solution. The ether was then shaken with solid calcium chloride and then distilled from phosphorous pentoxide. Fresh sodium was introduced into the distillate and the mixture allowed to stand until further reaction ceased. The ether was then distilled from fresh phosphorous pentoxide and fresh sodium introduced. This sodium gave no reaction so that the ether was considered anhydrous. As a matter of fact this was not strictly necessary as water was to be introduced from the gel.

The Method of Measurement:

A well purified gel which was perfectly white was allowed to adsorb water vapor until completely saturated. A little distilled water was added to make sure of complete filling of the pores. The excess moisture was removed by placing the gel on a fine grade of filter paper. The gel was then introduced into bulb A of the apparatus illustrated in Figure II. About 50 c.c. of the anhydrous ether were introduced into bulb A and shaken with the wet gel. Bulb A was then immersed in water cooled to 12°C. in a Dewar flask. The temperature of this was hand regulated and could be kept within 0.1°. The temperature



Water Solubility Apparatus

of 12° was chosen because the solubility of cadmium iodide in ether of various water contents had been determined at that temperature.

When equilibrium had been established dry air introduced through the tube on the top of bulb A forced the ether with the water it had dissolved over into Bulb B and onto the cadmium iodide. Bulb B was then placed in the Dewar flask and repeatedly shaken. A period of from two to three hours was allowed for equilibrium to establish itself. A calibrated pipette was used to remove a known amount of this solution from Bulb B. This was run into a small weighed glass evaporating dish and slowly evaporated to dryness on a hot plate. The residue was dried thoroughly and weighed. This was repeated to constant weight. This value gave the amount of CdI_2 dissolved in the etner solution. The values of the solubility of water in the ether could thus be accurately determined.

EXPERIMENTAL RESULTS.

The experimental results for the various samples of gel are given below. Figures III, IV, V, VI, VII and VIII present these facts graphically.

Experiment X.

4.145 g. gel 10 o/o H_2O 40° α = .285 1/n= .115

P	X	X′/M	Log. P	Log.(100 X′/M)
15.6	.435	.1009	1.19312	1.00389
30.65	.989	.2307	1.48603	1.36305
68.6	1.423	.3257	1.83632	1.51282
98.3	1.926	.44004	1.99255	1.64349
109.2	2.358	.5409	2.03822	1.73312
145.47	2.896	.6615	2.16277	1.82053

Experiment XII

3.74 g. gel 5.2 o/o H_2O 40° α = .702 1/n= .966

P	X	X′/M	Log. P	Log.(100 X′/M)
8.97	.218	.0557	.95279	.74586
20.67	.512	.1310	1.31543	1.11727
51.2	.740	.1890	1.49415	1.27646
4[illegible].14	1.153	.2943	1.69144	1.46879
74.1	1.537	.3901	1.86982	1.56118
7[illegible].17	2.054	.5267	1.89856	1.72156
118.17	2.519	.6401	2.07281	1.80625
156.0	2.804	.7056	2.19312	1.84556

Experiment XI

3.271 g. gel 2.2 o/o H_2O 40° $a = .837$ $1/n = .818$

P	X	X′/M	Log. P	Log.(100 X′/M)
12.48	.320	.0782	1.09621	.76492
27.3	.852	.1861	1.43616	1.15340
37.05	1.079	.1973	1.56879	1.29513
53.04	1.480	.2701	1.72460	1.43152
70.2	1.997	.3648	1.84634	1.56205
97.5	2.532	.4608	1.98900	1.66351
113.1	2.989	.54448	2.05346	1.73598

Experiment IV

4.350 g. gel 16 o/o H_2O 25° $a = 1.504$ $1/n = .713$

P	X	X′/M	Log. P	Log.(100 X′/M)
20.9	.589	.1301	1.32015	1.11428
30.3	.733	.1609	1.48144	1.20656
36.04	.882	.1936	1.55678	1.28691
47.27	1.053	.2301	1.67459	1.36192
58.5	1.217	.2651	1.76716	1.42341
68.26	1.802	.3970	1.83417	1.59879
75.47	2.054	.4531	1.87777	1.65619
114.6	2.781	.60988	2.06670	1.78525

Experiment II

5.347 g. gel 10 o/o H_2O 25° $\alpha = 1.525$ $1/n = .754$

P	X	X′/M	Log. P	Log.(100 X′/M)
5.64	.185	.0534	.75128	.72754
11.28	.364	.1051	1.05231	1.02160
20.48	.569	.1632	1.31133	1.21272
38.16	.872	.2479	1.58161	1.39428
45.79	1.106	.3155	1.66077	1.49900
63.6	1.483	.4221	1.80346	1.62542
127.2	2.222	.6220	2.10449	1.79379

Experiment VI

5.512 g. gel 5 o/o H_2O 25° $\alpha = 1.897$ $1/n = .796$

P	X	X′/M	Log. P	Log.(100 X′/M)
6.0	.408	.0729	.77815	.86273
13.06	.863	.1540	1.11594	1.18752
26.5	1.451	.2579	1.42325	1.41145
33.49	2.086	.3717	1.52492	1.57019
42.74	2.686	.4788	1.63083	1.68015
84.8	3.561	.6292	1.92840	1.79879

Experiment IX

4.452 g. gel 2.2 o/o H_2O 25° $\alpha = .7113$ $1/n = 1.075$

P	X	X′/M	Log. P	Log. X′/M
21.2	.873	.1909	1.32634	1.28081
25.4	1.052	.2299	1.40483	1.36154
30.74	1.309	.2863	1.48770	1.45682
33.92	1.531	.3355	1.53046	1.52569
38.8	1.798	.3943	1.58883	1.59583
48.76	2.184	.4785	1.68806	1.67988
60.42	2.626	.57489	1.78118	1.75958

Experiment XIII

3.140 g. Gel 5.2 o/o H_2O 10° α = 2.66 1/n= .8749

P	X	X′/M	Log. P	Log.(100 X′/M)
5.48	.436	.1368	.73878	1.13609
10.95	.690	.2158	1.03941	1.33405
15.33	1.113	.3552	1.18554	1.55047
21.13	1.502	.4706	1.32490	1.67265
27.35	1.932	.6053	1.43696	1.78197
48.51	2.387	.7426	1.68583	1.87075

Experiment XIV

3.301 g. Gel 10 o/o H_2O 10° α = 1.664 1/n= .942

P	X	X′/M	Log. P	Log.(100 X′/M)
10.95	.516	.1552	1.03941	1.19089
18.07	.860	.2543	1.25696	1.40535
23.54	1.226	.3663	1.37181	1.56027
35.04	1.924	.5708	1.54456	1.75648
65.7	2.326	.6819	1.81757	1.83372

The symbols used above are explained by the following:

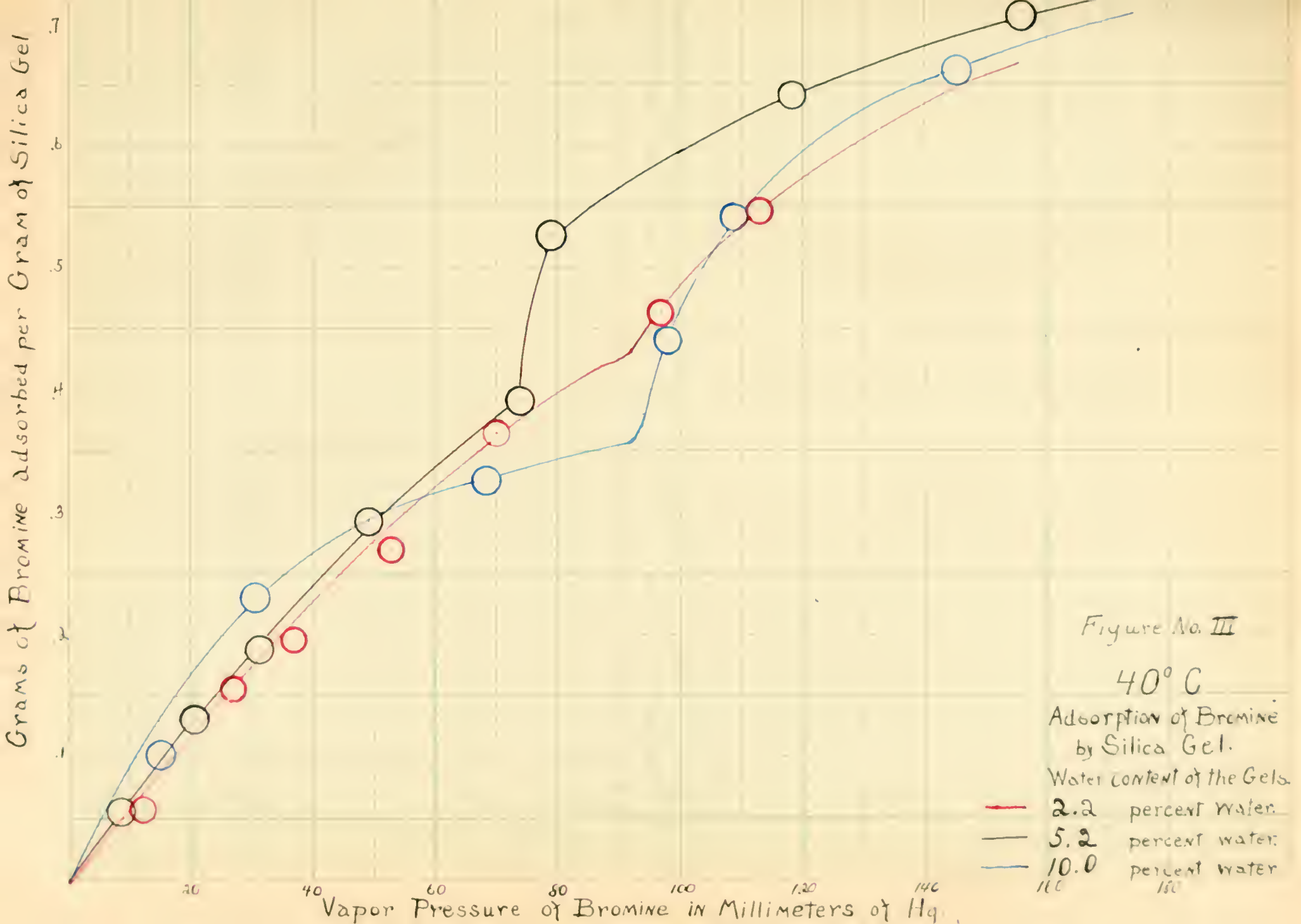
P = Vapor pressure of the bromine above the gel in tube A as calculated.

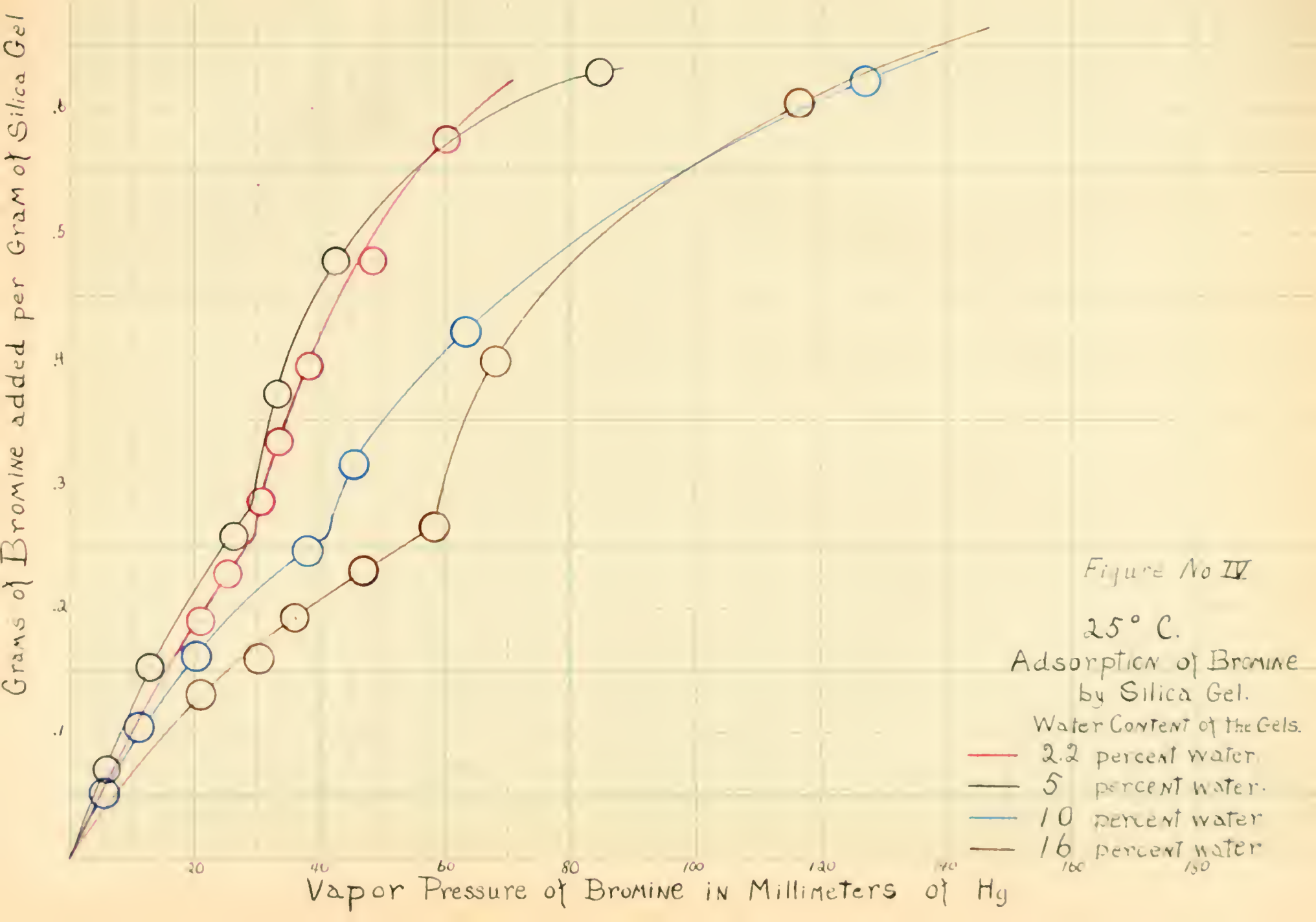
X = The weighed amounts of bromine added to tube A.

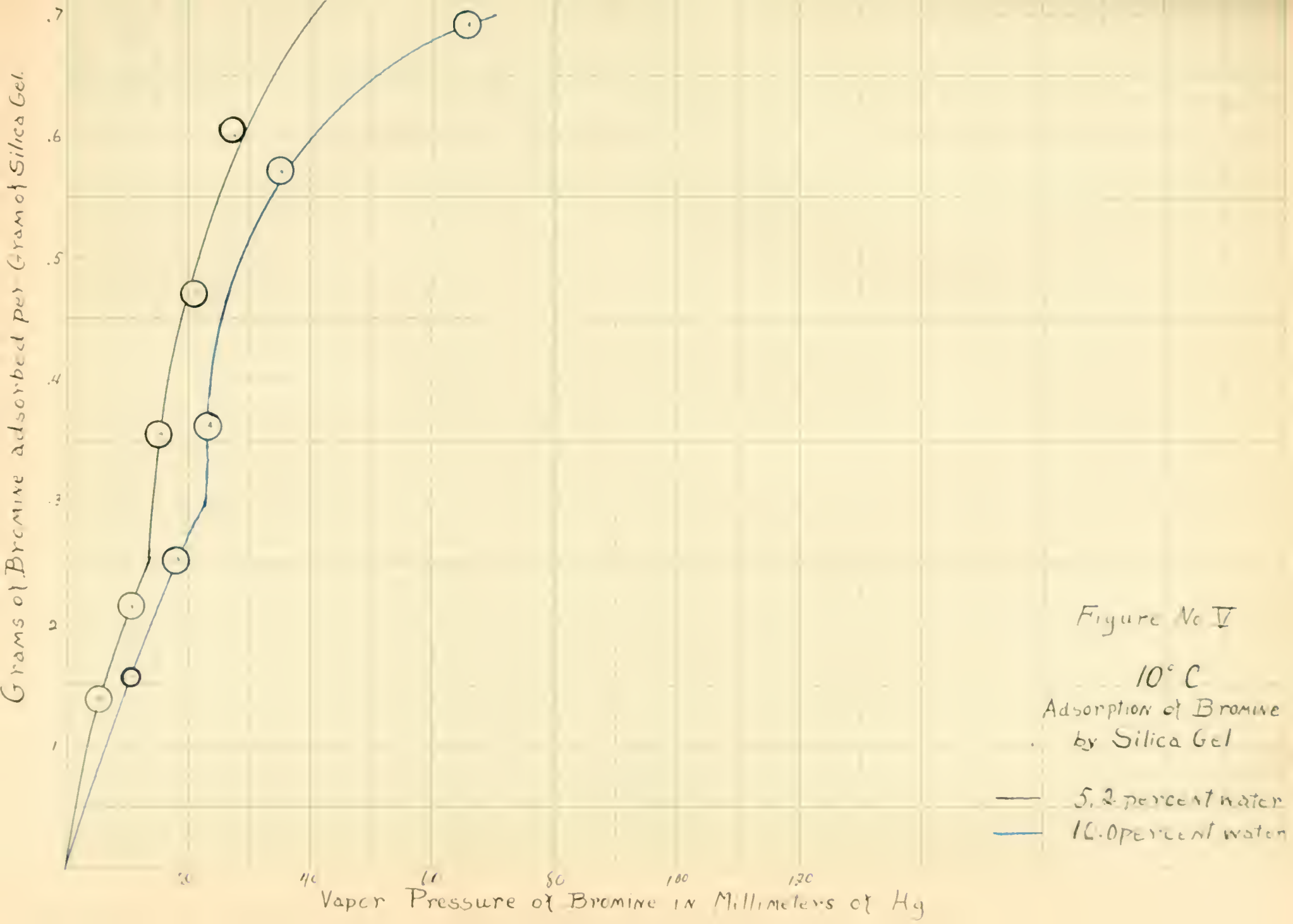
X′= The amount of bromine actually taken up by the gel.

M = The mass of the gel.

α and 1/n are the constants in the adsorption equation $x/m = \alpha p^{1/n}$


Grams of Bromine Adsorbed per Gram of Silica Gel
.7
.6
.5
.4
.3
.2
.1
20
40
60
80
100
120
140
160
180
Vapor Pressure of Bromine in Millimeters of Hg
Figure No. III
40° C
Adsorption of Bromine by Silica Gel.
Water content of the Gels.
2.2 percent water.
5.2 percent water.
10.0 percent water


Grams of Bromine added per Gram of Silica Gel
.6
.5
.4
.3
.2
.1
20
40
60
80
100
120
140
160
180
Vapor Pressure of Bromine in Millimeters of Hg
Figure No IV
25° C.
Adsorption of Bromine by Silica Gel.
Water Content of the Gels.
2.2 percent water
5 percent water.
10 percent water
16 percent water


Grams of Bromine adsorbed per Gram of Silica Gel.
.7
.6
.5
.4
.3
2
1
20
40
60
80
100
120
Vapor Pressure of Bromine in Millimeters of Hg
Figure No V
10° C
Adsorption of Bromine by Silica Gel
5.2 percent water
10.0 percent water

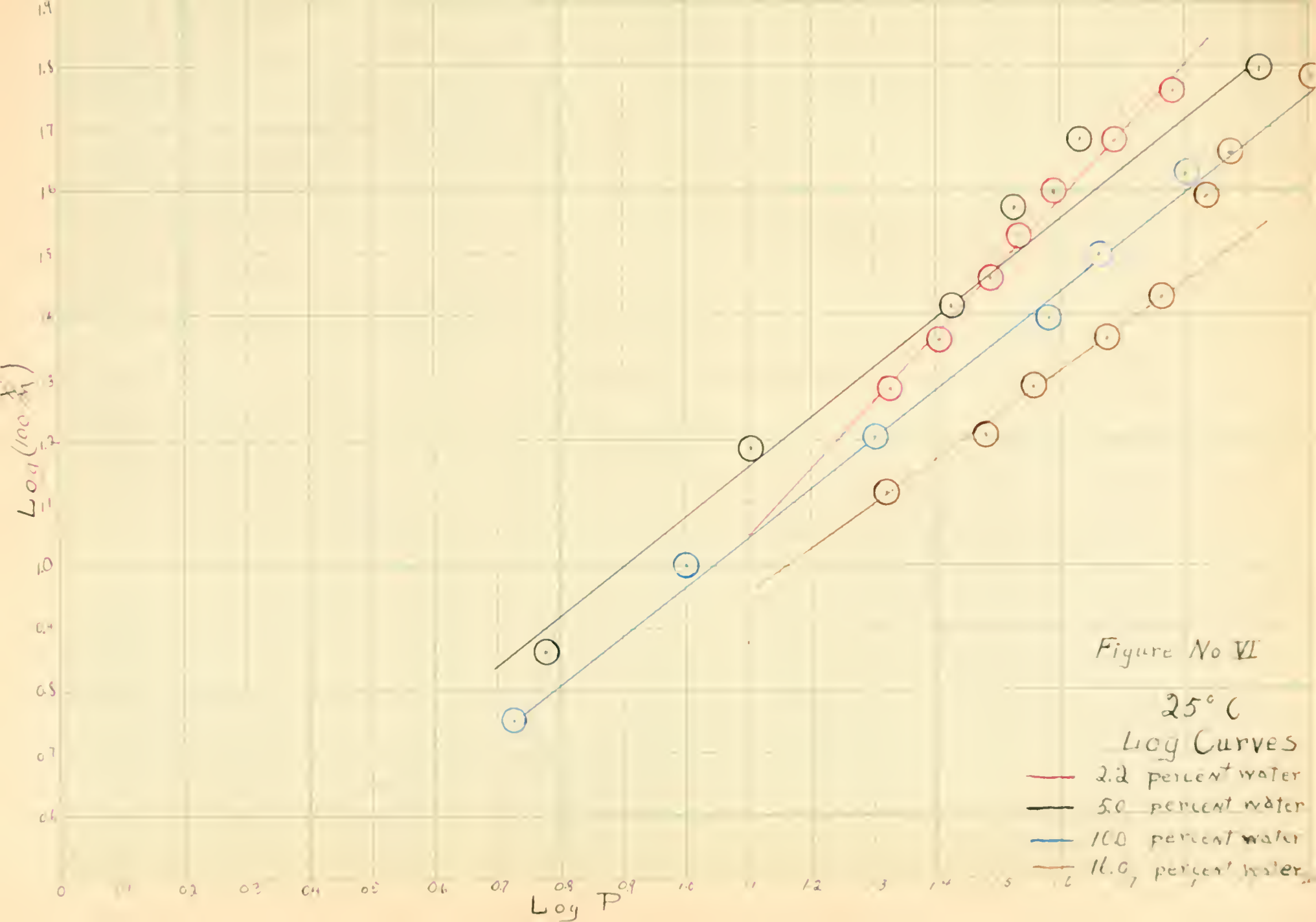

Log (100 x/m)
Log P
25° C
Log Curves
2.2 percent water
5.0 percent water
10.0 percent water
11.0 percent water

Figure No VI

RESULTS FOR THE SOLUBILITY OF WATER FROM THE SILICA GEL INTO ETHER.

The curve for the solubility of cadmium iodide in ether with various amounts of water present(Figure No. VII) was taken from the work of Dan Tyrer(6). From this curve the solubility of water from the gel into the ether could be determined once the amount of cadmium iodide in the ether had been determined.

Experiment No. 1 of this solubility work gave the following results:

Grams of CdI_2 dissolved per 100 gms. of solvent = 5.58g.

Grams of water per 100 of ether(read from curve) = .80g.

Saturation value at this temperature = 1.14g.

Per cent of saturation = 70.17

Experiment No. II

First extraction of ether:

Grams of CdI_2 per 100 gms. of solvent = 6.17

Grams of water per 100 of ether = .87

Per cent saturation = 76.31

Second extraction of ether:

Grams of CdI_2 per 100 gms. of solvent = 6.05

Grams of water per 100 of ether = .85

Per cent saturation = 74.56

Third extraction of ether:

Grams of CdI_2 per 100 gms. of solvent = 5.47

Grams of water per 100 of ether = .788

Per cent saturation = 69.12

Experiment No. III

First extraction of ether:

Grams of CdI_2 per 100 grams of solvent	=	4.38
Grams of water per 100 grams of ether	=	.695
Per cent saturation	=	78.51

Second extraction of ether:

Grams of CdI_2 per 100 grams of solvent	=	3.46
Grams of water per 100 grams of ether	=	.784
Per cent saturation	=	68.77

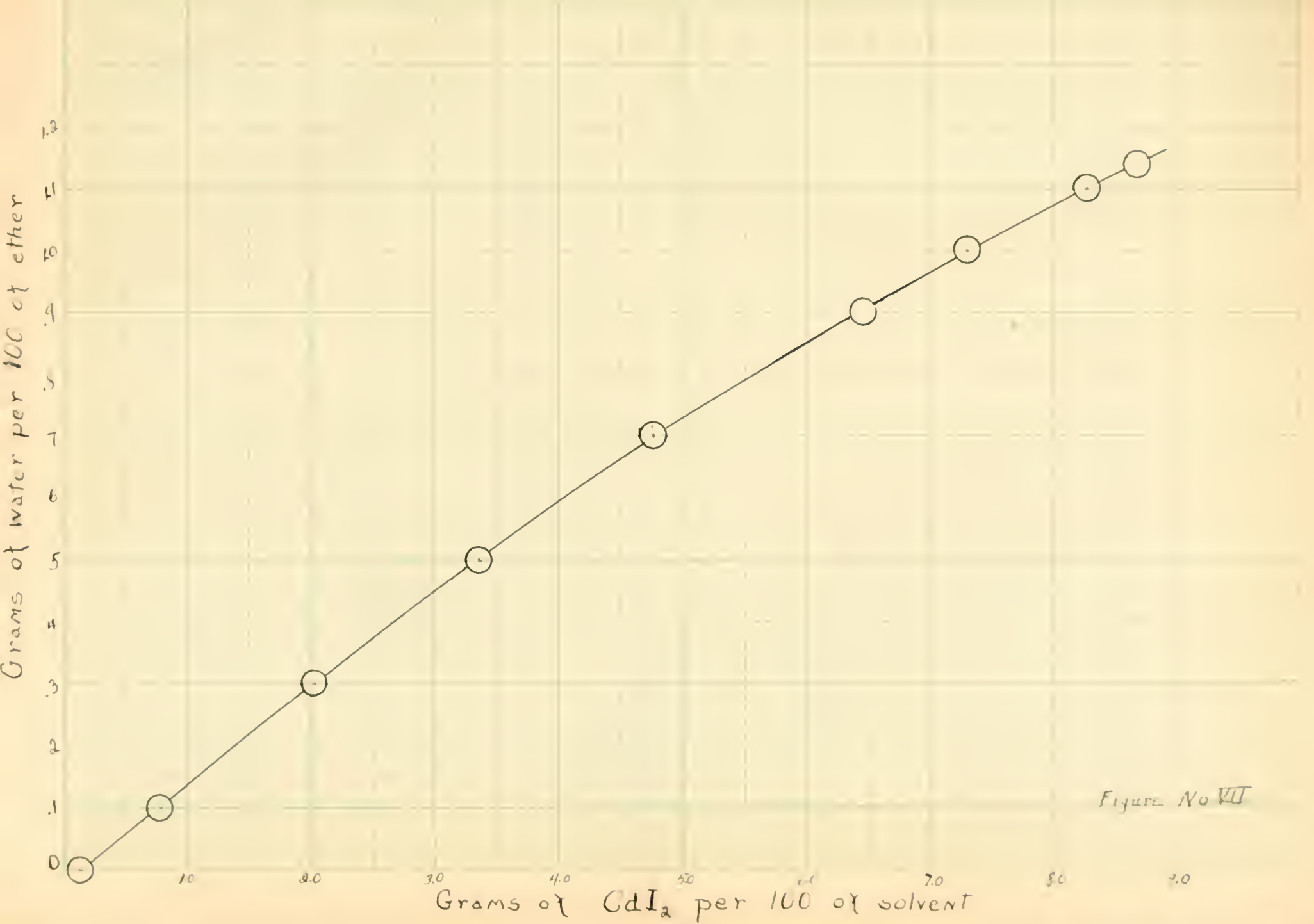


Figure No VII

DISCUSSION

It is evident from the curves obtained by plotting the values of X/M against those of P that for the adsorption of bromine by silica gel in the presence of air no such simple relation exists as was found by McIlavack and Patrick(7) for sulphurdroxide. The curves obtained are very similar to those obtained by Anderson(4) for alcohol and benzol, and by Patrick(5) for SO_2 and NH_3. From the nature of the experimental method air was of course present throughout the entire process of bromine adsorption. No doubt the presence of this air causes the break to occur in the curve. It is very probable that neither Anderson nor Patrick obtained the conditions of extreme evacuation which McIlavack and Patrick used.

If the well-known adsorption equation of Freundlich $X/M = \alpha P^{1/n}$ is used in the logarithmic form $\log. X/M = \log. \alpha + 1/n \log. P$, a straight line should result on plotting $\log. X/M$ against $\log. P$. The curves for bromine adsorption at 25°C. are given in Figure VI. It is evident from inspection that these curves are not rigidly straight lines. Bends occur in them at the same places as the bends occurred in the curves for X/M against P. Drawing an average straight line through the points it is possible to obtain an average value for α and $1/n$. The value of α is of course obtained when $P = 1$, or when $\log. P = 0$. The value of $1/n$ is the slope of the curve and can be easily evaluated once the value of α is known. The values thus evaluated are given in the tables of results.

In addition to showing the usual change in value with temperature change the values of α and $1/n$ vary with the gels used. The value of α is some function of the affinity between the surface and the vapor and we might well expect a change in this value with a change in the surface of the adsorbing material. However, as was previously noted the values are only average values and must of necessity be only approximate.

Since Figures III, IV and V show decided differences in the qualities of the various gels a calculation of the size of pore would show a difference. Anderson(4) has shown that the following equation holds very well for his work on silica gel.

$$\text{Log. } P_1 = \text{Log. } P_o - \frac{2TS\ 0.4343}{So\ Po\ r} \quad \text{or}$$

$$r = \frac{2TS\ 0.4343}{SoPo \log. \frac{Po}{P_1}}$$

Where

P_1 = Vapor pressure in the pores

Po = Ordinary vapor pressure of the liquid

T = Surface tension of the liquid

r = Radius of pore or capillary

δ = Density of the vapor

So= Density of the liquid

Using this equation the value of r for the gel of 15o/o water content and for the gel of 5o/o water content was calculated. The value of P_1 used was the value at the point of the break in the X/M - P curves. The value of Po was taken from the vapor pressure

curve for bromine obtained by Ramsay and Young(8). The values for T, S, and So were taken from Landolt and Bornstein. The value of r for the gel of 16o/o water content at 25°C. was found to be 1.4 x 10^{-7} c.m. The value of r for the gel of 5 o/o water content at the same temperature was found to be .8 x 10^{-7} c.m.

These values are considerably smaller than those found by Anderson and by Patrick. These values are only of relative significance. In all probability the equation does not hold in these regions of capillarity so that the absolute calculation of r is meaningless. The value of the density of the liquid used is the normal value at the temperature in question. This value for the density of the liquid in the pores is no doubt too large. Schavack and Patrick as well as other writers have shown that the liquid in the pores is dilated due to the pull of the surface film. In fact, the work of these authors indicates that the value of the tension on the liquid is exceedingly large.

The curves in Figures III, IV, and V show very clearly that a gel with less than 10 o/o water acts best as an adsorbing medium. However, the curves also show that below a certain value of water content the adsorptive power decreases, the gel of 2.2 o/o water content being less effective than the one of 5 o/o water. This may be due to a change in the actual capillary structure of the gel or it may be due to a partial sintering caused by the high temperature to which this gel was subject.

The explanation of the break in the adsorption isotherms due to the presence of air is not clear. It may be due to small bodies of trapped air which when subjected to the pull of the surface

film rise to the surface and escape. This would then allow increased adsorption without much change in the vapor pressure in the pores of the gel. As has been mentioned before other writers have calculated this dilation pull or tension and found it to be of the order of several hundred atmospheres. It does not seem at all improbable then that trapped air bubbles escape as this pull increases. It is highly improbable, however, that the air which actually covers the surface of the pores is removed in this way or that it is removed with a vacuum. The work of Langmuir(9) indicates that the single layer of adsorbed molecules is held very strongly.

The results on the solubility of water from the silica gel are far more interesting and have much greater theoretical importance. As was mentioned before Hulett(10) has shown that barium sulphate is more soluble when finely divided than it is when the particles are relatively large. Hulett and also Ostwold showed from thermodynamical considerations that the results of this solubility study were to be expected.

The thermodynamical considerations are based on the theory of the vapor pressure of small drops. Lord Kelvin was the first to recognize the fact that the vapor pressure of a liquid is dependent on the magnitude and shape of the surface. Let us calculate the work dw which can be obtained by allowing the mass dm of a liquid with surface tension σ, and whose density is g, to evaporate from a sphere of radius

r to a plane surface. The mass m of the sphere is $4/3\ \pi\ r^3 s$ and its surface a is $4\ \pi\ r^2$. When the mass of the small sphere of liquid is diminished by dm, its surface is diminished by da, and we gain the amount of work σ da. If we take the mass dm of the liquid from the small sphere and add it to a large mass of the same liquid whose surface is a plane, that is a sphere of infinite radius, the area of the plane surface will not be altered appreciably. The work done in the addition of the small amount dm to the large sphere is therefore zero. The total work done, dw = σ da, can be calculated with the aid of the following equations:

$$m = 4/3\ \pi\ r^3 s \qquad (1)$$

$$dm = 4\pi r^2 s\,dr \qquad (2)$$

$$a = 4\pi r^2 \qquad (3)$$

$$da = 8\pi r\ dr \qquad (4)$$

Substituting the value of dr from (2) in (4) we have

$$da = \frac{2}{rs}\ dm \qquad (5)$$

From which it follows that

$$dw = \frac{2\sigma}{rs}\ dm \qquad (6)$$

The same amount of work may be obtained reversibly in a different manner by considering the isothermal distillation of the amount dm from the small sphere to the plane surface. Let P be the ordinary vapor pressure of the liquid at the plane surface and P' its vapor pressure at the small sphere. If the vapor obeys the gas laws it follows from the Second Law that the

work done in the transference is

$$dw = \frac{RT}{M} \ln \frac{p'}{p} \, dm, \qquad (7)$$

where M is the molecular weight of the vapor.

Combining equations (6) and (7) the following relation is obtained:

$$\ln \frac{P'}{P} = \frac{2\sigma}{rs} \frac{M}{RT} \qquad (8)$$

or the value of $\ln \frac{p'}{p}$ is greater than zero.

The vapor pressure at a convex surface is therefore greater than the vapor pressure at a plane surface. In a similar way it may be shown that the vapor pressure at a concave surface is less than at a plane surface. For concave surfaces equation(8) would become

$$\ln \frac{P}{P'} = \frac{2\sigma}{rs} \frac{M}{RT} \qquad (9)$$

if this approximation $\ln \frac{P}{P'} = \frac{P - P'}{P'}$, is justified, equation(9) may be written as follows:

$$P = P'\left(1 + \frac{2\sigma}{rs} \frac{M}{RT}\right) \qquad (10)$$

Applying the Vant Hoff theory for solutions concentration may be substituted giving

$$C = C'\left(1 + \frac{2\sigma}{rs} \frac{M}{RT}\right) \qquad (11)$$

Equation (11) shows that materials are more soluble from a plane surface than from a concave surface. The effect is very small until molecular dimensions are reached. At ordinary temperature (300°) with $r = 10^{-5}$ the effect is about 1 o/o.

However, the investigations on silica gels have all demonstrated the extreme fineness of the pores. They approach molecular dimensions. The gel thus offers an ideal medium for testing out this law provided of course the liquids in the pores of the gel wet the walls of the capillaries. As previously mentioned the solubility of bromine in water from these gel pores was tested. The surface tension effect of water was sufficient to force the bromine out of the gel. The investigation then turned to the use of water as the medium to be dissolved from the gel. Surface tension effects dictated this course of proceedure.

The results of the solubility of water from the gel into ether justify the course of reasoning exceedingly well. At no time during the series of three experiments was the solubility of water from the gel, the normal solubility of water in ether. In every experiment there was at least ten times as much water present in the gel as was necessary to saturate the ether completely. Yet as succeeding portions of ether were added and, after attaining equilibrium, removed, it was found that the solubility of the water was gradually decreasing. This can be explained by assuming that the greatest diameter of the capillary occurrs at the surface of the gel. The diameter decreases in value as the capillary penetrates deeper and deeper into the gel. This decreasing size of capillary accounts very well for the decrease in solubility. Had the experiments been carried out still further the solubility of the water would no doubt have decreased until finally

the water would have shown a zero solubility. Time did not permit this in the above experiments.

The chief objection which will be made to the experimental results will be that equilibrium had not become fully established. In order to answer this objection the time for extraction in Experiment II was purposely made about twice as long as in Experiment III. The results indicate no apparent difference in solubility in the two cases.

A sample of the ether used was saturated with water at 12°C. and the solubility of the CdI_2 determined in this sample. The results showed that the CdI_2 was if anything more soluble in the ether used than the results of Tyrer show. This indicates that the solubilities as determined from the curve are higher than the actual solubilities themselves since Tyrer's values for saturation were used in calculating the percentage solubility.

Experimental results thus prove the thermodynamics of concave surfaces. Furthermore, these results clearly prove that the liquids in the capillaries of silica gel actually wet the walls of the small tubes. Otherwise, no concave surfaces would exist to give the observed results.

CONCLUSION.

1. The adsorption of bromine by silica gel was measured at 40°, 25° and 10°.

2. The maximum efficiency was found to occur with gels having about five per cent water.

3. Smooth curves are never obtained in the presence of air and an explanation of this fact is offered.

4. The solubility of water from the pores of silica gel was measured in anhydrous ether at 12°.

5. The marked lessening of the solubility of the water from the gel over that of water from a plane surface was shown. This experimentally proves the thermodynamical considerations of concave surfaces.

6. It was definitely shown that the liquids in the pores of the gel actually wet the surface of these pores.

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AUTOBIOGRAPHY.

The author was born May 1, 1893 at Lawson, Minnesota, completing his secondary education at that place. He entered Carleton College, Northfield, Minnesota, in September 1911, and was graduated with the A. B. degree in June 1915. Entering the University of Illinois in the fall of 1915 as a graduate student in chemistry the author received the degree of Master of Arts in Chemistry in June 1917. In November of the same year he entered the service of the Government as a research chemist in War Gas Investigations, later receiving a commission as Second Lieutenant in the Chemical Warfare Service of the Army. After the signing of the Armistice, he was honorably discharged from the service and thereupon matriculated in the Graduate School of Johns Hopkins University, Baltimore, Maryland.

Together with H.C. Holman et. al. he has published, in the Journal of the American Chemical Society, two short papers on the Physical Chemistry of Smokes. This work was done in the War Laboratories at Washington, D.C.